

Translation

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[Kokai] No.: **Heisei 11-79733**

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(21) Patent Application [Tokugan] No.: Heisei 9-237056	(72) Inventors: Tetsuya Iwao, et al.
(22) Filing Date: September 2, 1997	(71) Assignee: Nippon Alkyl Aluminum KK

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(54) Title of the Invention: Method of Preparation of Sodium Borohydride

**Scope of Patent Claims**

Claim 1

A method of preparation of sodium borohydride comprising a process for reacting (A) sodium hydride or sodium aluminum hydride and (B) trialkyl borate in a hydrocarbon solvent while stirring, wherein a polishing medium is added to the foregoing solvent while continuing to stir.

### Claim 2

The method of preparation of sodium borohydride according to Claim 1 wherein the foregoing polishing medium consists of ceramic or metallic spherical particles 0.5 mm to 10 mm in diameter.

### Claim 3

A method of preparation of sodium borohydride comprising a process for reacting (A) sodium hydride or sodium aluminum hydride and (B) trialkyl borate in a hydrocarbon solvent while stirring wherein a homogenizer is used for the stirring.

### Claim 4

The method of preparation of sodium borohydride according to Claim 3 wherein the RPM level for the foregoing homogenizer is set to maintain a fresh solid surface on the foregoing sodium hydride or sodium aluminum hydride.

### Claim 5

The method of preparation of sodium borohydride according to Claim 3 wherein the foregoing homogenizer is operated at an RPM level of 500 to 20,000 RPM.

### Details of the Invention

#### Area of Industrial Application

The present invention relates to a method of preparation of sodium borohydride, a useful reducing agent.

#### Prior Art

Processes are known to the art for reacting sodium hydride and trimethyl borate in a liquid hydrocarbon solvent to produce sodium borohydride. For example, as disclosed in U.S. Patent 2,720,444.

#### Problems To Be Resolved by this Invention

The problem with the foregoing method is that yields are low and have poor reproducibility. As was described in Japan Patent Sho 47-49440, when the heating method, stirring method and speed, dropwise addition method and rate, and post addition operations were all held constant, the yields of the sodium borohydride were not constant. The present inventors confirmed this fact through follow-up experimentation. We found that when using conventional stirring methods in

reacting sodium hydride or sodium aluminum hydride with trialkyl borate in a hydrocarbon solvent, the reaction yields were low and exhibited poor reproducibility.

#### Means Used To Resolve the Problems

The present inventors inferred that the following was responsible for the low yields of sodium borohydride. To wit, both the sodium borohydride and the sodium alkoxide, which is produced as a by-product, are solids, and both tend to adhere to the surface of the reaction starting material of solid sodium hydride, which diminishes the contact between the sodium hydride and the liquid trimethyl borate, which in turn causes lower yields.

Based upon this line of thinking, they discovered that introducing high shear forces into the dispersion system during stirring dramatically improved yields, and this discovery resulted in the completion of the present invention.

To wit, the present invention provides a method of preparation of sodium borohydride comprising a process for reacting (A) sodium hydride or sodium aluminum hydride and (B) trialkyl borate in a hydrocarbon solvent while stirring wherein a polishing medium is added to the foregoing solvent while continuing to stir.

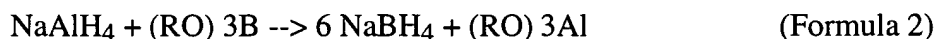
It additionally provides a method of preparation of sodium borohydride comprising a process for reacting (A) sodium hydride or sodium aluminum hydride and (B) trialkyl borate in a hydrocarbon solvent while stirring, wherein a homogenizer is used to effect stirring.

#### Implementation Embodiment of the Invention

There are two types of reactions that may be used according to this invention, as shown in (Formula 1) and (Formula 2).



To wit, sodium hydride and trialkyl borate are reacted to synthesize sodium borohydride and sodium alkoxide.



To wit, sodium aluminum hydride and trialkyl borate are reacted to synthesize sodium borohydride and aluminum trialkoxide.

The metal hydrides used in this invention, i.e., sodium hydride and sodium aluminum hydride, are solid powders which may be used in this method of preparation even if some impurities are present. Commercially available hydrides may be used as well. The alkyl group of the trialkyl borate used in this invention should be a straight-chain or branched alkyl group with 1

to 6 carbon atoms. Specific examples include a methyl group, ethyl group, n-propyl group, isopropyl group, n-butyl group, cyclobutyl group, n-pentyl group, n-hexyl group, etc. The following advantages derive from the use of *tert*-n-butyl borate. That is, the by-product of aluminum *tert*butoxide produced by the reaction can be subjected to hydrolysis to recover the n-butanol for reuse. Since n-butanol does not readily dissolve in water, it may be easily isolated and recovered.

Examples of reaction solvents include saturated hydrocarbons such as n-hexane, cyclohexane, n-heptane, decane, flowing paraffin, etc.; or aromatic hydrocarbons such as benzene, toluene, xylene, decalene, tetralene, etc. The reaction should also be implemented in an inactive environment of nitrogen, argon or the like. There are no particular restrictions upon the reaction temperature, but normally it is performed at 200 to 300°C.

With regard to the order for adding the reaction reagents, normally, the sodium hydride or sodium aluminum hydride powder is suspended in the solvent and then, while stirring, the trialkyl borate is added, either as is or dissolved in a solvent. However, this procedure may also be reversed.

Next, the stirring methods used during the reaction that are characteristic of this invention will be further described.

First, the method that involves the addition of a polishing medium and stirring will be explained. In this case, an autoclave type of reactor would normally be used to implement the reaction, and that vessel would be equipped with mechanical stirring means such as propeller blades, and optionally, suitable baffles. The polishing medium would then be added to the apparatus.

The polishing medium used in this invention is composed of spherical particles which can impact the solids in the reaction system to effectively crush them during the reaction. Examples include ceramics such as glass, silica, or alumina spheres, or metals such as iron, SUS, etc. The diameter should range from about 0.5 mm to 10 mm, preferably from 2 mm to 5 mm. Using this size of polishing medium results in excellent crushing effects when the medium collides with the reaction solids. The amount of the polishing medium used would vary according to the concentration of the reaction starting materials in the hydrocarbon solvent, but normally, it should range from 10 to 50 vol. %

To explain the effects of the polishing medium in this invention in greater detail, the addition of the polishing medium and the stirring during the reaction causes the surface of the solids in the system to remain fresh, inasmuch as the SBH and the by-product sodium alkoxide or aluminum alkoxide produced when the liquid trialkyl borate reacts with the surface of the sodium hydride or sodium aluminum hydride tends to tightly adhere to the surface when formed. This abrading to expose a fresh surface allows the liquid trialkyl borate to continue to react smoothly with the reaction solids and for high yields to be obtained in a stable manner.

Next, stirring with a homogenizer will be described in greater detail. This method produces effects similar to those obtained by adding a polishing medium and stirring.

A homogenizer is a stirring apparatus that imparts high shear forces to the dispersion system, it is comprised of stirring blades and a cylinder containing them, and the shear forces are imparted to the dispersion between the two.

The RPM range for the homogenizer operations would depend upon the shape of the blades, the clearance between the blades and the other cylinder and the like, but normally, the operation should be performed at from 5,000 to 20,000 RPM. For stirring, the speed would vary according to the size of the reaction vessel, size of the blades, amount of polishing media, and amount of reactants and solvents, but normally homogenation should be performed at 50 to 5,000 RPM.

In this invention, the trialkyl borate should be added at a rate which will not unduly increase the temperature of the reaction solution, normally it should be added over the course of 0.5 to 10 hours. After the addition, the reaction should be continued for another 0.5 to 10 hours.

Following the reaction, the reaction solution is in a suspension state, but the reaction solvent can be separated by filtration. Next, the residual solids can be extracted with liquid ammonia, an amine such as isopropylamine; an alcohol such as isopropyl alcohol or the like, to purify the sodium borohydride. At that time, it may be recrystallized for further purification or spray-dried into appropriately sized granules.

### Examples

Examples will be presented below to further describe the invention, but the invention is not confined to these examples.

#### Example 1

Under a flow of inactive gas, 120 mL of beads (3 mm) and 48 g (2 moles) of sodium hydride were added to 300 g of flowing paraffin and dispersed while stirring at  $265 \pm 5^\circ\text{C}$ , and then 52 g (0.5 mole) of trimethyl borate was added dropwise over a 30-minute period. After the addition, the temperature and stirring were maintained for an additional hour.

After chilling the dispersion, it was filtered and the solids were washed in hexane before drying under a flow of inactive gas. Of the 100 g of solids, 16.3 g of sodium borohydride were recovered. This represented a stoichiometric yield of 86.1%. Then, the product was extracted with isopropyl amine to obtain a 5.8 g of purified product, 83.5% stoichiometrically. Analysis revealed the purity to be 99.3%.

#### Comparative Example 1

The same operation was performed but without adding the beads. After purification 8.5 g of sodium borohydride were obtained, a yield of 45%. Purity was 97.3%.

### Example 2

48 g (2 mole) of sodium hydride was dispersed in 300 g of flowing paraffin under a flow of inactive gas to prepare a dispersion, which was maintained at  $265^{\circ}\text{C} \pm 5^{\circ}\text{C}$  and stirred at 10,000 RPM in a homogenizer while 52 g (0.5 mole) of trimethyl borate was added dropwise over a 30-minute period. After the addition, stirring and temperature were maintained for an additional hour. After cooling, the solids were filtered and washed with hexane, and then dried under a flow of inactive gas. 100 g of the solids contained 15.3 of sodium borohydride, 80.8% of the theoretical yield. Next, isopropylamine was used for extraction to obtain 14.8 g of purified product, 78.2% of stoichiometric yield. The purity was 99.2%.

### Example 3

120 mL of beads (3 mm diameter) and 27 g (0.5 mole) of sodium aluminum hydride were dispersed in 300 g of flowing paraffin under a flow of inactive gas. While stirring at  $265 \pm 5^{\circ}\text{C}$ , 114.9 g (0.5 mole) of tributyl borate was added dropwise over a 30-minute period. After the addition, the stirring and temperature were maintained for an additional hour.

After cooling, the suspension was filtered and the solids washed in hexane before drying under a flow of inactive gas. Among the 142 g of solids, there was 16.4 g of sodium borohydride, which was 86.6% of theoretical. Isopropylamine extraction was performed to obtain 16.1 g of purified product, a stoichiometric yield of 85.1%. Purity was 99.3%.

### Effects of the Invention

As described above, the method of this invention of adding a polishing medium or stirring with a homogenizer during the reaction to prepare sodium borohydride resulted in stable and much higher yields than were obtainable by the prior art.

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